

Sensitivity of a Chemical Mass Balance model to different molecular marker traffic source profiles

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5 **Sensitivity of a Chemical Mass Balance Model to**
6 **Different Molecular Marker Traffic Source**
7 **Profiles**
8

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25 **ABSTRACT**

26 Use of the Chemical Mass Balance (CMB) model for aerosol source apportionment requires the
27 input of source profiles of chemical constituents. Such profiles derived from studies in North
28 America are relatively abundant, but are very scarce from European studies. In particular, there is a
29 lack of data from European road vehicles. This study reports results from a comparison of road
30 traffic source profiles derived from (1) US dynamometer studies of individual vehicles with (2) a
31 traffic profile derived from measurements in a road tunnel in France and (3) new data derived from
32 a twin-site study in London in which concentrations at an urban background site are subtracted from
33 those measured at a busy roadside to derive a traffic increment profile. The dynamometer data are
34 input as a diesel exhaust, gasoline exhaust and smoking engine profile, or alternatively as just a
35 diesel exhaust and gasoline exhaust profile. Running the CMB model with the various traffic
36 profiles together with profiles for other sources of organic carbon gives variable estimates of the
37 contribution of traffic to organic carbon and to PM_{2.5} concentrations. These are tested in two ways.
38 Firstly, unassigned organic carbon in the output from the CMB model, assumed to be secondary
39 organic carbon, is compared to secondary organic carbon estimated independently using the
40 elemental carbon tracer method. Secondly, the estimated traffic contribution to organic carbon and
41 PM_{2.5} is compared with an estimate derived simply from the measured elemental carbon
42 concentrations, and the effect on aerosol mass closure is investigated. In both cases the CMB
43 model results correlate well with the independent measures, but there are marked differences
44 according to the traffic source profile employed. As a general observation, it appears that the use of
45 dynamometer data with inclusion of a smoking engine profile has a tendency to over-estimate
46 traffic emissions at some sites whereas the tunnel profile shows a tendency to under-estimate.
47 Overall, the traffic profile derived from the twin-site study gives probably the best overall estimate,
48 but the quality of fit with independent estimates of secondary organic carbon and traffic particle
49 mass depends upon the site and dataset for which the test is conducted.

50 **Keywords:** Receptor models; CMB; source profile; traffic emissions; particulate matter

51

1. INTRODUCTION

Road traffic is one of the key urban air pollution sources, and in the last few decades a significant amount of research has been undertaken in order to understand the emission characteristics as well as processes that govern vehicular emissions (Shi and Harrison, 1999; Charron and Harrison, 2003; Lough et al., 2007; Phuleria et al., 2007; El Haddad et al., 2009; Pant and Harrison, 2013). A good understanding of the relative contribution of traffic to ambient air pollutant concentrations, especially particulate matter (PM) is vital for policy action. Source apportionment techniques are used widely for quantitative estimation of the contribution of different sources to ambient PM concentrations and can be implemented in many different ways, receptor modelling being one of the methods. Watson and Chow (2007) describe receptor models as models that “interpret measurements of physical and chemical properties taken at different times and places to infer the possible or probable sources of excessive concentrations and to quantify the contributions from those sources” and this category of source apportionment techniques includes microscopic and chemical models (Pant and Harrison, 2012). With the assumption that the concentrations of chemical species are preserved between sources and receptors, receptor models use the principle of mass conservation for apportionment of PM mass to different air pollution sources. Thus, the concentration of a species measured in a sample of particulate matter can be described as (Hopke, 1991):

$$X_{ij} = \sum_{p=1}^p g_{ip} f_{pj} \quad (1)$$

where X_{ij} is the species concentration of i in the sample j , g_{ip} is the fractional mass of species i in source p and f_{pj} is the mass contribution of source p to particulate matter in ambient air in sample j . There are several receptor models such as the Chemical Mass Balance (CMB) model, multivariate statistical models such as Principal Component Analysis (PCA) including factor analysis models such as Positive Matrix Factorization (PMF), Multilinear Engine (ME), and UNMIX) and hybrid

77 models such as Constrained Physical Receptor Model (COPREM) (Watson et al., 2002; Viana et
78 al., 2008). Different models use different approaches to solve equation 1, for e.g., the CMB model
79 uses the effective-variance least squares method whereas UNMIX uses eigenvector analysis.

80

81 **1.1 CMB Model**

82 The CMB model uses the ambient measurement data for chemical species together with the
83 associated uncertainty and source profiles for different sources as inputs, and the output consists of
84 estimates of the contribution of each source to the total mass. The model has several assumptions
85 including non-reactivity of the chemical species and non-co-linearity of the source profiles (Watson
86 et al., 2002). In addition, the number of species should be greater than the number of sources in
87 order to derive results from the model. This model has been used extensively for source
88 apportionment of PM mass (Schauer et al., 1996; Bi et al., 2007; Sheesley et al., 2007; Chelani et
89 al., 2008; Lambe et al., 2009; Stone et al., 2010; Yin et al., 2010; El Haddad et al., 2011; Hanedar et
90 al., 2011; Rutter et al., 2011; Guo et al., 2012; Perrone et al., 2012). A large number of markers can
91 be used for source apportionment including elemental carbon (EC), organic carbon (OC), trace
92 metals and organic molecular markers. However, trace metals such as Fe, Cu, Zn and Ni are often
93 emitted from several key sources, and in some cases, it is difficult to apportion PM mass to the
94 sources based on the trace metals alone (Lin et al., 2010). In addition, with removal of species such
95 as Br and Pb from fuels, such markers cannot be used conclusively for source apportionment
96 analyses. With the idea that molecular marker compounds are emitted by specific sources and can
97 be used to distinguish between PM sources, Schauer et al. (1996) proposed CMB modelling using
98 organic molecular markers (hereafter referred to as CMB-MM). A number of source-specific
99 organic molecular markers have since been proposed for use in CMB modelling. Key molecular
100 markers include levoglucosan for wood burning, hopanes and steranes for vehicular emissions,
101 higher n-alkanes for vegetative detritus, benzothiazoles for tyre wear and cholesterol and lactones
102 for cooking (Rogge et al., 1993a,b; Schauer et al., 1996; Lough et al., 2007; Heo et al., 2013). A

103 detailed description of various organic markers for different sources has been compiled by Lin et al.
104 (2010).

105

106 **1.2 Source Profiles**

107 Selection of appropriate source profiles is one of the critical steps towards obtaining a good fit with
108 the CMB model. Source profiles are defined as “the mass abundances, i.e. fraction of total mass of
109 chemical species in source emissions, and such profiles are generally representative of source
110 categories rather than individual emitters” (Watson et al., 2002). Such profiles are created using
111 emission samples from a range of emitters of a particular source category and conducting physical
112 and chemical analyses to arrive at the contributions of each tracer element/compound (Watson et
113 al., 2002). Source profiles are used for identification and quantification of contributions of different
114 sources to PM using the CMB model as well as to compare and validate results obtained from factor
115 analysis models (e.g. PMF) and to a large extent the model relies on the accuracy of the source
116 profiles used as an input. However, in the absence of locally relevant source profiles, the Source
117 Contribution Estimates (SCE) can be prone to erroneous results. In recent years, significant
118 differences have been observed between laboratory-tested and real world mixed source traffic
119 emissions (Gertler et al., 2002; Yan et al., 2009; Ancelet et al., 2011). While the typical components
120 of any source profiles are found to be more-or-less similar, the relative mass abundances vary based
121 on location and emitter characteristics. As a result, different combinations of source profiles can
122 provide statistically valid yet completely different solutions (Robinson et al., 2006a).

123

124 Traffic emission profiles can be generated using several different methods including lab-based
125 dynamometer studies, tunnel studies and twin-site studies (Rogge et al., 1993a; Lough et al., 2007;
126 He et al., 2008; El Haddad et al., 2009; Yan et al., 2009). Since the twin site/tunnel measurements
127 are carried out in the ambient environment, and for a mixed fleet, they are seen to be more
128 representative of real-world emissions. A number of papers have reported the estimation of the

129 contribution of traffic emissions to total PM or a component of PM using twin-site studies (Yan et
 130 al., 2009; Bukowiecki et al., 2010; Gietl et al., 2010; Oliveira et al., 2010; Pey et al., 2010). With
 131 the assumption that all sources other than traffic (including any local or regional sources) have the
 132 same impact at both roadside and a nearby background site, the increment at the roadside site
 133 obtained using the equation 2 is used as a local traffic increment estimate (Harrison, 2009; Yan et
 134 al., 2009; Wang et al., 2010).

$$\text{Concentration of } X_{\text{traffic}} = \text{Concentration of } X_{\text{roadside}} - \text{Concentration of } X_{\text{background}} \quad (2)$$

135

136 The aim of this paper is to assess the response of the CMB model to molecular marker profiles for
 137 traffic derived using different sampling approaches. Tests of the model are summarised in Figure 1.
 138 Traffic source contribution estimates (SCEs) of PM_{2.5} OC as well as PM_{2.5} mass generated from
 139 CMB using different traffic profiles were compared with the traffic estimates obtained using
 140 elemental carbon as a tracer (Pio et al., 2011). The estimated Secondary Organic Carbon (SOC)
 141 derived from CMB was compared to SOC calculated using the method proposed by Castro et al.
 142 (1999).

143

144

145 **2. METHODS**

146

147 **2.1 Air Sample Collection and Analysis**

148 PM_{2.5} samples were collected in Birmingham in 2007-2008 and in London (United Kingdom) in the
 149 years 2010 (summer) and 2011 (winter) respectively. The urban background site in Birmingham
 150 was located in an open field within the University of Birmingham campus. The site is about 3.5 km
 151 southwest of the centre of Birmingham and the nearest anthropogenic sources are a nearby railway
 152 and some moderately trafficked roads. The rural site is located about 20 kilometres west of
 153 Birmingham at a distance of about 200 metres from the A451, a moderate to heavily-trafficked
 154 road. The site is surrounded by unused land/grass. The urban background site in London was
 155 located in a residential area in West London at a distance of 10 metres from the road. The site is

located 7 kilometres to the west of central London and is located in a cabin within a school campus where equipment from the national Automatic Urban and Rural Network is also hosted. The roadside site was located on the kerbside of a heavily trafficked (ca. 80,000 vehicles per day) six lane highway (Marylebone Road) running through a street canyon in central London. The sampling station is located at a distance of 1 metre from the road at height of 3 metres. The site is located opposite the Madame Tussauds Museum and is surrounded by residential and commercial buildings. Further site details for Birmingham and London are available in Yin et al. (2010) and Gietl et al. (2010) respectively. PM_{2.5} samples were collected on 150 mm quartz fibre filters using Digitel high volume samplers (DHA-80) in summer and winter seasons for a period of 24 hours in London. In Birmingham, 24 hour PM_{2.5} samples were collected for the first 5 days of every month on 20 cm x 25 cm quartz fibre filters using a Tisch TE-6070 high volume sampler. In addition, 24 hour PTFE filter samples (PM₁₀ and PM_{2.5}) were also collected at all sites using a collocated dichotomous Partisol sampler. OC and EC were measured using the Sunset Laboratory Thermal-Optical Carbon Analyser, molecular markers including hopanes, straight-chain alkanes, PAHs and levoglucosan were measured using GC-MS (Agilent GC-6890N plus MSD5973N) and Al and Si were measured using WD-XRF (Philips[®] MAGIX-PRO automatic sequential wavelength dispersive X-ray Fluorescence spectrometer). Ions (SO₄²⁻, NO₃⁻, Cl⁻) were measured using ion chromatography (Dionex ICS-2000). The detailed sampling and chemical analysis methodology is presented in Yin et al. (2010) and Harrison and Yin (2010). Only PM_{2.5} samples were used for this study.

175

176 **2.2 CMB Model**

177 The CMB 8.2 model from USEPA was used for the estimation of source contribution to PM_{2.5}-OC. 178 Six key sources were included in the model runs including vegetative detritus (Rogge et al., 1993b), 179 wood smoke (Fine et al., 2004; Sheesley et al., 2007), natural gas (Rogge et al., 1993c), coal 180 combustion (Zhang et al., 2008), road dust (Chow et al., 2003) and traffic. Species used in the data 181 analysis include elements (Al, Si), n-alkanes (C25-C35), hopanes (trisnorhopane, hopanes,

182 norhopane), PAHs (benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, picene,
183 indeno[123-cd]pyrene, benzo[ghi]perylene) and levoglucosan.

184

185 Winter samples from the roadside and urban background sites in London were used for preparation
186 of the source profile while the samples from the Birmingham sites (n= 28 for each site) and the
187 summer samples from the urban background site (n= 30) in London were used for the CMB
188 analysis.

189

190 Model outputs were evaluated using several different parameters. As a first step, goodness-of-fit
191 parameters, r^2 and χ^2 values were checked and a chi-square value less than 4 and r^2 value between
192 0.8-1.0 were considered acceptable. T-stat values (ratio of the source contribution estimate and
193 standard error) were used to determine the significance of a particular source and a value less than 2
194 indicates that the source is at or below detection limit. Other parameters included the species' C/M
195 ratio (i.e. ratio between calculated and measured concentration) and R/U ratio (i.e. ratio of signed
196 difference between calculated and measured concentration, i.e. residual divided by standard error,
197 i.e. uncertainty) with acceptable values ranging between 0.75-1.5 and -2 to +2 respectively. Species
198 that did not fit within the range were removed from subsequent runs but a base number of species
199 were always included to ensure that the number of species is more than the number of sources. The
200 MPIN (modified pseudo inverse normalized) matrix was used as a diagnostic tool to identify the
201 influential species for each source type with influential species showing values between 0.5 to 1
202 (Chow et al., 2007).

203

204

205

206

207 **2.3 Source Profiles**

208 *Profile derived from twin-site data*

209 To prepare a dimensionless profile for PM requires calculation of the ratio of each of the species
210 with respect to PM concentration for the same location (Landis et al., 2007). In this study, a similar
211 approach was used, and since we are assuming the difference between the roadside and background
212 site to be the traffic increment (as in equation 2), the formula has been modified accordingly
213 (equation 3).

$$\text{Source profile value}(X) = \frac{X_{\text{roadside}} - X_{\text{background}}}{OC_{\text{roadside}} - OC_{\text{background}}} \quad (3)$$

214

215 Table 1 presents the source profile that was prepared using this approach derived from
216 measurements at the heavily-trafficked Marylebone street canyon site (Galatioto and Bell, 2013)
217 and the typical urban background site of North Kensington (Bigi and Harrison, 2010). The species
218 mean value represents the species source profile value and standard deviation refers to the profile
219 uncertainty. Daily winter campaign samples (n = 26) were averaged to obtain the profile and the
220 average standard error was used as source profile uncertainty. A similar approach has been reported
221 by Yan et al. (2009) for preparation of a traffic profile for Georgia, USA. The traffic mix on
222 Marylebone Road is broadly representative of UK traffic (see Table S1 in Supplementary
223 Information). It is important to note that this profile was generated based on a select group of
224 organic markers, and the unique site characteristics at the roadside site (Marylebone Road) in
225 London might have introduced some bias in the results.

226

227 Uncertainty for the various organic species in the profile was observed to be much higher compared
228 to other published real-world and lab-based profiles. Similar observations of high uncertainties in
229 ambient data have been reported by Yan et al. (2009) and Peltier et al. (2011) and may reflect in
230 part, different traffic mixes on different days as well as higher uncertainties associated with ambient
231 sampling.

232 *Tunnel profile*

233 This was derived from measurements in a road tunnel in France reported by El Haddad et al.
234 (2009). The profile (Table 1) was prepared by normalizing the species concentration in PM_{2.5}
235 against OC concentration in PM_{2.5} to get concentration in terms of species/μg of organic carbon.
236

237 *Dynamometer profiles*

238 Separate source profiles for gasoline, diesel and smoking engines were taken from the work of
239 Lough et al. (2007) derived from measurements of emission from US vehicles made using
240 dynamometers.
241

242 **3. RESULTS AND DISCUSSION**

243 **3.1 Comparison of Source Profile with other Published Profiles**

244 Concentrations of most of the organic markers are broadly similar across the ambient data profiles
245 with the exception of PAHs for which the tunnel profile from France reported lower PAH
246 concentrations than roadside profiles from the UK and USA (Figure 2). This may be related to the
247 very high uptake of diesels in France. However, the freeway measurement of Phuleria et al. (2007)
248 appear to suggest higher emissions from diesel vehicles. The dynamometer gasoline profile was
249 observed to be very similar to the profiles derived from ambient data.
250
251

252
253 Ambient concentration data for hopanes from London and Birmingham were compared with a wide
254 range of traffic profiles using ratio-ratio plots. Such plots are defined as ‘scatter plots of ratios
255 constructed with data from three species, i.e. two species (which are the target species) whose
256 values are normalized using the third reference species’ (Robinson et al., 2006a). While the
257 aggregation of the ambient data around a point signifies that CMB can produce a good result with a
258 single source profile, distribution of data along a diagonal line indicates the need for at least two
259 distinct profiles for good results. Plotting the source profiles with ratio-ratio plots using specific
260 markers can be useful for determination of the most relevant source profiles and such plots have

261 been used previously for comparison of ambient data with source profiles (Subramanian et al.,
262 2006; Dutton et al., 2009; Gao et al., 2011).

263

264 Ambient data for hopanes and EC from London and Birmingham were plotted together with source
265 profiles derived from laboratory dynamometer studies, as well as real-world mixed traffic emissions
266 collected from the literature (Schauer et al., 1999; Watson et al., 1998; Schauer et al., 2002; Lough
267 et al., 2007; El Haddad et al., 2009; Yan et al., 2009) in Figure 3. The composite traffic profile was
268 found to be significantly different from lab-generated source profiles for both the background and
269 roadside sites, while the comparison with other ambient traffic profiles revealed a similarity
270 between ambient measurement data and ambient profiles, although the uncertainty (expressed as
271 standard deviation of daily data) is typically much higher for ambient profiles (Figure 3). The
272 differences between the profiles were smaller in the case of homohopanes and bishomohopanes.
273 Differences among the various profiles can be attributed to changes in vehicle technology over time
274 and the dynamic fleet mix. Significant differences in the source profiles have been reported for
275 different vehicle categories (Kim Oanh et al., 2010). Use of different sampling and analytical
276 protocols may also have an influence.

277

278 The ambient air data in the case of hopane-EC plots generally fit to a straight line, suggesting a
279 variable mixture of two sources, presumably reflecting gasoline and diesel vehicles. However the
280 huge difference in concentrations between the ambient air data and the majority of the
281 dynamometer profiles is unexplained. The diesel dynamometer profiles generally appear to be to
282 the left of the gasoline profiles, but lie in a totally different region of the plot to the ambient air data.
283 This may relate to the rapidly evolving technology of diesel vehicles, and the different vehicle types
284 studied. In particular, the reductions in smoke emissions, and hence EC, from diesels will have led
285 to increased hopane/EC ratios in newer vehicles

286 **3.2 CMB Sensitivity Analysis**

287

288 3.2.1 *Estimation of traffic particle mass and mass closure*

289 Chemical profiles measured in London (2010 summer data) and Birmingham (2007 data) were
 290 analysed using the CMB model to calculate source contributions to PM_{2.5} OC with the aim of
 291 comparing the sensitivity of the model to different types of traffic profiles. Three different traffic
 292 profiles were tested, i.e. dynamometer profiles for diesel, gasoline and smoking engines (hereafter
 293 referred to as DYN) (Lough et al., 2007), a twin-site London profile (hereafter referred to as TWIN)
 294 and a France tunnel profile (hereafter referred to as TUN) (El Haddad et al., 2009). The smoking
 295 engine profile used in the analysis includes off-road engines and Lough and Schauer (2007)
 296 reported smoker profiles to impact the estimation of source contribution from gasoline, diesel and
 297 smoker vehicles. In order to understand the contribution from the smoking engine profile, two
 298 analyses were conducted for the DYN profile: gasoline and diesel engine only (DYN-GD) and
 299 gasoline, diesel and smoking engines (DYN-A). For comparison, the average data from each of the
 300 sites was also run with a traffic profile consisting of 80% of the concentrations of the chemical
 301 species measured at the roadside site in London (hereafter referred to as R80). For coal combustion,
 302 wood combustion and road dust, a number of source profiles were tested initially to choose the best
 303 profile for the ambient measurement data and the selected profiles were then used together with
 304 different traffic profiles to obtain final results. A number of different source profiles were run and
 305 the statistical outputs such as standard error and the ratio between calculated/measured values were
 306 assessed for each profile.

307
 308 Based on equation 4, “Other OC” was calculated which is the OC unaccounted for by primary
 309 sources, and taken to represent secondary OC (SOC) (Yin et al., 2010).

$$Other\ OC = Measured\ OC - \sum SCEs\ (primary\ sources) \quad (4)$$

310
 311 Several other authors have also used the same approach and have also assumed the “Other OC” to
 312 be SOC (Subramanian et al., 2007; Docherty et al., 2008; Stone et al., 2009). Source contributions

313 to PM_{2.5} mass were then calculated using ratios of PM_{2.5} mass/PM_{2.5} OC for each source applied to
314 the PM_{2.5}-OC SCEs obtained using CMB modelling as detailed in Yin et al. (2010). These were
315 added to estimates of contributions from other sources (marine aerosol, sulphates, nitrates) using
316 factors from the Pragmatic Mass Closure Model (Harrison et al., 2003) to test overall PM_{2.5} mass
317 closure.

318

319 In the CMB model, r^2 and χ^2 values were observed to be between 0.96-1.00 and 0.02- 2.70
320 respectively. Only the species with C/M ratio (ratio between calculated and measured
321 concentration) between 0.75-1.5 and R/U ratio (ratio of signed difference between calculated and
322 measured concentration, i.e. residual divided by standard error, i.e. uncertainty) between -2- +2
323 were used for the model runs. In addition, any profiles with a negative source contribution or a t_{stat}
324 <1 were removed from subsequent runs and markers for the different sources were monitored using
325 the MPIN matrix available in the CMB model runs and were cross-validated with published marker
326 data (Table S2, Supplementary Information).

327

328 In the case of the daily data, although overall correspondence was observed between CMB runs
329 using DYN and TWIN and TUN in terms of identification of sources and OC mass attribution, there
330 were variations in certain cases with higher or lower attribution of a source. In some cases,
331 however, while for one model, a source was deemed insignificant (t -stat value < 2), the other
332 models showed it as a significant source. It is important to note that a t_{stat} value >2 indicates 95% or
333 more confidence in the estimates.

334

335 Results for apportionment of OC appear in Figure 4. Across all scenarios, the total traffic
336 contribution to OC varied as DYN-A> TWIN> DYN-GD> TUN. The DYN-A profile attributed
337 more OC to vehicles (including off-road engines) than the DYN-GD, TWIN and TUN profile.
338 However, at both the urban background and rural sites in Birmingham, the results were comparable

339 between DYN-A and TWIN profiles and DYN-GD and TUN profiles. Interestingly, while the
340 TWIN profile used benzo(ghi)perylene as the key marker for traffic, the TUN profile used EC as
341 the key marker. In the case of DYN profiles, EC, hopanes and benzo(ghi)perylene were observed to
342 be the key markers for diesel, smoking and gasoline engines respectively. In the case of the London
343 data, the DYN-A scenario causes the primary sources in the model to account for > 100% of OC
344 without any SOC, which is clearly implausible. In the Birmingham data, the choice of profile does
345 not impact greatly on the outcome. The R80 profile produced very similar results to the TWIN
346 profile (Table 2; Figure 4). The traffic SCEs using TUN and DYN-A and DYN-GD were also
347 compared against the traffic SCE using TWIN profile, and while good correlation was observed for
348 urban background sites ($r^2 > 0.75$), the correlation was much weaker in case of the rural site ($r^2 \sim$
349 0.25-0.35).

350

351 When mass closure of $PM_{2.5}$ is attempted including other major sources using the coefficients
352 reported by Harrison et al. (2003), closure is generally good, especially for the Birmingham data
353 (Figure 5). The DYN-A attributes a larger $PM_{2.5}$ mass to road traffic than the other profiles,
354 especially in the London data. Predictably, as for OC results, the total $PM_{2.5}$ mass apportioned to
355 traffic varied as DYN-A > TWIN > DYN-GD > TUN. Overall mass closure is good for both urban
356 and rural sites and winter and summer seasons (Table 2). Results for the R80 profile are not
357 discussed for $PM_{2.5}$ since very similar SCEs were observed for this profile compared to the TWIN
358 profile

359

360 The CMB/Pragmatic Mass Closure Model resolved the PM mass reasonably well with all profiles
361 with 89.8- 129.7% of $PM_{2.5}$ mass resolved across all data sets (Table 2, Figures 4 and 5) and the
362 DYN-GD profile models the highest percentage mass across all sites. In general, all the CMB
363 models (based on dynamometer profiles and the composite profiles) were able to apportion
364 approximately similar OC mass, although dynamometer-based profiles apportioned a higher

percentage of OC mass to traffic. Subramanian et al. (2007) postulated that over-apportionment of OC mass can occur either due to missing primary sources or due to sampling artifacts. Between the three profiles, the lowest total OC mass was attributed by the TUN profile runs across all sites. In terms of resolution of the traffic source, CMB runs with dynamometer and composite profiles showed some differences. If only gasoline and diesel sources are considered (i.e. using DYN-GD), the TWIN profile had the maximum mass apportioned to the traffic source and the TUN profile had the minimum mass apportioned to traffic. However, with the inclusion of the smoking engine profile in DYN set of profiles, DYN-A apportioned the highest mass to the traffic source. Further, the t_{stat} values for the DYN-A ($t_{\text{stat}} > 5$ across all cases for diesel and smoking engine profiles) and TUN ($t_{\text{stat}} > 6$ across all cases) profiles were consistently higher than the TWIN model (t_{stat} between 2-3 in most cases). The lowest standard error was recorded for the DYN profiles (A & GD) which correlates with the lower uncertainties associated with these profiles. Higher uncertainties in the case of TWIN and TUN profiles can be attributed to the errors associated with ambient measurements. Between the TWIN and TUN profiles, the standard error was lower in the case of the TUN profile. In some cases, the t_{stat} for the traffic and gasoline had a value of less than 2 in the case of TWIN and DYN (A & GD) profiles respectively rendering the traffic source insignificant. No runs had $t_{\text{stat}} < 2$ for traffic in the case of the TUN profile. The R80 profile, run as a test yielded results very similar to the TWIN profile (Table 2; Figure 4).

The MPIN matrix data for runs was also analysed to assess and cross-compare the influential species (defined as species with a value > 0.7 in the matrix) for the different traffic profiles. While in the case of DYN profiles (A & GD), the same markers (EC for diesel engine, hopanes for smoking engine and benzo(ghi)perylene for gasoline engine, value = 1 across all runs) were consistently found to be influential across all runs, different species were recorded as influential in the case of the TWIN and TUN profiles. Overall, the TWIN profile showed a value of 1 for benzo(ghi)perylene across the runs and the TUN profile showed a value of 1 for EC. In both cases, the other key sets of

391 markers, i.e. EC and hopanes were found to be influential across most runs. Similar results were
392 reported by Chow et al. (2007). There were cases, however, where EC and/or trisnorhopane were
393 over- or underestimated, and in those cases, the key marker varied. Benzo(ghi)perylene and hopane
394 were estimated correctly in most cases. For the TUN profile, n-alkanes (A25 and 26) were also
395 recorded as influential species in some cases. Interestingly, in the case of TUN profile runs,
396 interference between the vegetative detritus and traffic profile was observed, and in many runs, the
397 vegetative detritus SCE was insignificant or zero although positive SCEs were recorded using
398 TWIN and DYN (A & GD) profiles. In a CMB sensitivity study, Sheesley et al. (2007) observed
399 the biomass profile to impact the contribution estimate for traffic. Test runs were then conducted
400 with the TUN profile excluding the n-alkane data, but the SCEs for traffic were found to be more or
401 less similar to the original runs. The Other OC mass and the total mass apportioned, however,
402 changed slightly as a result of positive SCEs for vegetative detritus. Lower percentages of mass
403 were apportioned to traffic during the summer season by the model with both types of profile.
404 Similar observations have been reported for the USA (Subramanian et al., 2007; Bullock et al.,
405 2008) and Europe (El Haddad et al., 2011) where SOC has been reported to be higher in the
406 summer season due to increased photochemical activity. Also, a higher percentage of SOC was
407 estimated for the rural site compared to the urban background sites, which is also reflected in the
408 higher OC/EC ratio for the rural site.

409

410 **3.3.2 Comparison of CMB traffic estimates with an estimate based upon EC**

411 Assuming road traffic to be the dominant source of EC, traffic emission estimates were obtained for
412 PM_{2.5}-OC and PM_{2.5} mass using EC*0.35 and EC*1.35 respectively based on Pio et al. (2011). The
413 traffic SCE outputs for PM_{2.5}-OC and PM_{2.5} from the CMB model with different traffic profiles
414 were compared against the EC traffic emission estimates (Table 3). The most similar estimates for
415 primary vehicular emissions were observed for DYN-GD with the estimates being highly correlated
416 ($r^2 > 0.85$) with the traffic estimates obtained using EC for the Birmingham sites. For DYN-A, the

dynamometer profiles produced a much higher estimate for the traffic contribution and this was due to a high SCE for the smoking engine profile. However, not all of that SCE is necessarily derived from road traffic as the source profile for the smoking engine includes off-road vehicles which are a significant contributor to $PM_{2.5}$ in the UK (AQEG, 2012). Poor correlation was observed for all the profiles at the rural Birmingham site with correlation coefficients ranging between 0.26-0.41. The estimates obtained using the TWIN profiles showed similar correlation with the EC estimate compared to the estimates from the TUN profile.

424
425
426

3.2.3 Comparison of estimates of SOC

Organic carbon can be present in the atmosphere as primary organic carbon (POC) (directly emitted) or SOC (formed by atmospheric chemistry). Generation of SOC source profiles is rendered difficult due to the complex chemistry of secondary organic aerosol formation (Bullock et al., 2008) and diversity of composition. As a result, while the CMB model works well for attribution of POC sources such as biomass combustion and traffic, it is not able to apportion SOC due to lack of availability of appropriate source profiles (Stone et al., 2009; Guo et al., 2012; Schauer and Sioutas, 2012). Consequently, as in Yin et al. (2010), the CMB model was run to account for known primary sources of OC, and the difference between the sum of POC and measured total OC was attributed to SOC.

436

EC is released directly into the atmosphere and can be used to estimate relative amounts of primary and secondary OC. One of the simplest approaches involves use of the ratio between OC and EC. Higher OC/EC ratios are expected in the conditions where SOC is dominant and the highest OC/EC ratios are reported in rural and remote sites (Pio et al., 2011). The EC-tracer method involves the use of EC as a tracer for POC, allowing SOC to be calculated (Turpin and Huntzicker, 1995; Castro et al., 1999; Lee and Russell, 2007; Sheesley et al., 2007; Pio et al., 2011). Minimum ratios of OC/EC are taken as representative of primary OC (although they may be an over-estimate (Pio et

444 al., 2011)) and OC above that ratio is taken to be SOC. The method as outlined by Castro et al.
445 (1999) was used (equation 5) and estimates of daily SOC were made for each of the sites.

$$\text{Secondary OC} = \text{Total OC} - (\text{EC} \times (\text{OC/EC})_{\min}) \quad (5)$$

446

447 The quality of fit between the estimates of SOC from the CMB model and the EC tracer method
448 was evaluated by regression analysis (Table 4). Given that the EC tracer method is liable to under-
449 estimate SOC (Pio et al., 2011), an excess of “Other OC” over SOC might be expected, but in most
450 cases the “Other OC” is similar to, or less than the SOC. In the Birmingham (urban background),
451 London (urban background-summer) and Birmingham (rural) datasets, the three estimates are in
452 broad agreement.

453

454 **4. CONCLUSIONS**

455

456 It is evident from Figure 2 that traffic profiles of molecular markers measured in the field show
457 generally broad agreement. However, as Figure 3 shows, where plotted as normalised abundance
458 (marker/EC), the field data can differ by orders of magnitude from dynamometer data, and the
459 variation between dynamometer studies is typically greater than that between field measurements.
460 Perhaps surprisingly, both, however, give broadly similar estimates of traffic PM_{2.5} mass. Those
461 from the composite profile (TWIN) are probably better, as judged from the estimates from the EC
462 tracer method, and the mass closures. Correlations of the traffic estimates using the TWIN profile
463 against those obtained using EC were broadly similar to those obtained using the DYN (A & GD)
464 profiles. The estimates from TUN profile, however, were much more weakly correlated,
465 particularly at the rural site. This could be due to the interference between the traffic and vegetative
466 detritus sources for TUN model runs as explained in the previous section. It is possible that other
467 tunnel profiles more representative of the UK might perform better. It was also observed that
468 selection of species for inclusion in the profile can determine the overall modelling output, both for
469 estimation of the traffic source and the overall model output.

470

471 Based on the current analysis, it can be concluded that both the dynamometer and composite (twin-
472 site) profiles can provide reasonable estimates of the traffic contribution. In cases where
473 dynamometer profiles are not available, composite profiles can be used to estimate traffic
474 contribution to OC or PM mass. However, it is important to bear in mind that the high uncertainty
475 associated with the composite traffic profile can impact upon CMB model output since the model
476 takes into account both the profile uncertainty and the ambient data uncertainty. Further, traffic
477 source profiles based on ambient data can cause mis-apportionment of other sources since similar
478 compounds are often reported from different sources, for e.g. PAHs from different combustion
479 sources. Thus, it is important to select species for the profile in such a way that interference with
480 other sources would be minimal. Another consideration for the use of ambient data for preparation
481 of source profiles is the impact of oxidation of marker species in the atmosphere (Robinson et al.,
482 2006b). This can also impact the model output as it is assumed that the species are chemically
483 stable.

484

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763 **TABLE LEGENDS**

764

765 Table 1: Source composition profile for traffic based on twin sites from London (this study),
 766 tunnel site from France (El Haddad et al., 2009) and 80% of concentration data from
 767 the roadside site in London (this study) (all values in $\mu\text{g}/\mu\text{g}$ of OC)

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769 Table 2: Traffic mass estimate ($\mu\text{g}/\text{m}^3$) and total percentage (%) explained using different
 770 traffic profiles for (a) OC and (b) $\text{PM}_{2.5}$

771 Table 3: Comparison of the traffic estimates from the CMB model with the traffic estimate
 772 obtained using EC

773 Table 4: Comparison of the other OC estimate from the CMB model with the SOC estimate
 774 obtained using EC tracer method

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778 **FIGURE LEGENDS**

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780 Figure 1: Assessment of model performance using different metrics.

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782 Figure 2: Comparison of London profile with other traffic and dynamometer profiles (TWIN-
 783 Our profile; TUN- El Haddad et al. (2009); TWIN US- S &W- Yan et al., 2009;
 784 DYN-D, G &S- Lough et al., 2007).

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 787 dynamometer studies using ratio-ratio plots.

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800 **tunnel site from France (El Haddad et al., 2009) and 80% of concentration data from the**
801 **roadside site in London (this study) (all values in $\mu\text{g}/\mu\text{g}$ of OC)**

Compound	TWIN (mean \pm s.d.)	TUN (mean \pm s.d.)	R80 (mean \pm s.d.)
EC	1.600 \pm 1.440	2.72 \pm 0.49	1.620 \pm 1.440
Trisnorhopane	0.00005 \pm 0.00004	0.00010 \pm 0.00001	0.00007 \pm 0.00004
Norhopane	0.000200 \pm 0.00017	0.00036 \pm 0.0005	
Hopane	0.00014 \pm 0.00012	0.00027 \pm 0.0005	0.00016 \pm 0.00010
(S+R) Homohopanes	0.00020 \pm 0.00018	0.00028 \pm 0.00004	0.00026 \pm 0.00015
(S+R) Bishomohopanes	0.00030 \pm 0.00025	0.00010 \pm 0.00002	0.00036 \pm 0.00021
(S+R) Trishomohopanes	0.00028 \pm 0.00022	0.00008 \pm 0.00002	0.00029 \pm 0.00018
Benzo(ghi)perylene	0.000080 \pm 0.000055	0.000003 \pm 0.0000002	0.00011 \pm 0.00006

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Table 2: Traffic mass estimate ($\mu\text{g}/\text{m}^3$) and total percentage (%) explained using different traffic profiles for (a) OC and (b) $\text{PM}_{2.5}$

(a) OC

Site (season)	OC mass apportioned to traffic					Total % OC mass apportioned				
	DYN-A	DYN-GD	TWIN	TUN	R80	DYN-A	DYN-GD	TWIN	TUN	R80
Urban background site, London (Summer)	1.87	0.73	1.63	0.58	1.63	102	67.5	68.0	35.1	68.0
Urban background site, Birmingham	1.63	0.80	1.29	0.64	1.29	73.2	43.2	63.2	39.5	63.1
Urban background site, Birmingham (Summer)	1.43	0.69	1.15	0.58	1.15	61.4	37.5	53.5	34.6	53.5
Urban background site, Birmingham (Winter)	1.91	0.89	1.93	0.74	1.93	90.6	50.1	94.1	46.1	94.1
Rural site, Birmingham	1.33	0.55	1.21	0.48	1.01	77.1	46.3	75.6	42.3	67.7
Rural site, Birmingham (Summer)	1.34	0.44	1.21	0.67	1.21	79.2	48.3	71.3	52.0	75.6
Rural site, Birmingham (Winter)	1.26	0.66	1.10	0.48	1.10	76.2	48.1	70.5	39.4	70.5

(b) $\text{PM}_{2.5}$

Site (season)	$\text{PM}_{2.5}$ mass apportioned to traffic					Total % $\text{PM}_{2.5}$ mass apportioned				
	DYN-A	DYN-GD	TWIN	TUN	R80	DYN-A	DYN-GD	TWIN	TUN	R80
Urban background site, London (Summer)	2.98	1.61	2.69	0.96	2.69	123	130	119	122	119
Urban background site, Birmingham	2.61	1.61	2.13	1.61	2.13	104	108	106	97.5	106
Urban background site, Birmingham (Summer)	2.39	1.50	1.90	1.50	1.90	108	111	109	100	109
Urban background site, Birmingham (Winter)	2.93	1.70	3.18	1.70	3.18	94.7	101	98.1	89.9	98.1
Rural site, Birmingham	2.06	1.13	2.00	0.80	1.67	111	116	113	116	114
Rural site, Birmingham (Summer)	1.97	0.89	2.00	2.00	2.00	119	113	122	124	121
Rural site, Birmingham (Winter)	2.07	1.36	1.81	0.79	1.81	101	106	103	106	103

Table 3: Comparison of the traffic estimates from the CMB model with the traffic estimate obtained using EC

Site (season)	OC		PM _{2.5}	
	r ²		r ²	
Urban background, London (Summer)				
DYN-GD	0.99	y = 1.28x + 0.01	1.00	y = 0.75x + 0.01
DYN-A	0.94	y = 1.45x + 1.04	0.98	y = 0.80x + 1.24
TWIN	0.71	y = 1.55x + 0.37	0.71	y = 0.66x + 0.60
TUN	0.84	y = 0.61x + 0.29	0.84	y = 0.26x + 0.48
Urban background, Birmingham (Summer)				
DYN-GD	0.87	y = 1.31x + 0.00	0.95	y = 0.76x - 0.03
DYN-A	0.78	y = 2.37x + 0.33	0.89	y = 1.09x + 0.37
TWIN	0.67	y = 1.93x + 0.14	0.67	y = 0.83x + 0.23
TUN	0.73	y = 0.79x + 0.14	0.73	y = 0.34x + 0.23
Rural, Birmingham (Summer)				
DYN-GD	0.97	y = 1.21x - 0.00	0.92	y = 0.73x - 0.10
DYN-A	0.41	y = 1.12x + 0.88	0.61	y = 0.71x + 0.91
TWIN	0.26	y = 1.00x + 0.55	0.26	y = 0.43x + 0.91
TUN	0.16	y = 0.32x + 0.37	0.16	y = 0.14x + 0.62

Note: y = CMB model estimate; x = estimate derived from EC concentration

Table 4: Comparison of the Other OC estimate from the CMB model with the SOC estimate obtained using EC tracer method

Site (season)	r ²	
<i>Urban background, London (Summer)</i>		
DYN-A	0.81	y = 0.92x - 0.69
TWIN	0.70	y = 0.83x + 0.07
TUN	0.73	y = 0.80x + 0.74
<i>Urban background, Birmingham (Summer)</i>		
DYN-A	0.92	y = 0.86x - 0.52
TWIN	0.91	y = 0.86x - 0.10
TUN	0.90	y = 0.90x + 0.49
<i>Rural, Birmingham (Summer)</i>		
DYN-A	0.76	y = 0.79x - 1.22
TWIN	0.69	y = 0.73x - 0.71
TUN	0.92	y = 0.88x - 0.67

Note: y = CMB model estimate; x = estimate from EC tracer method

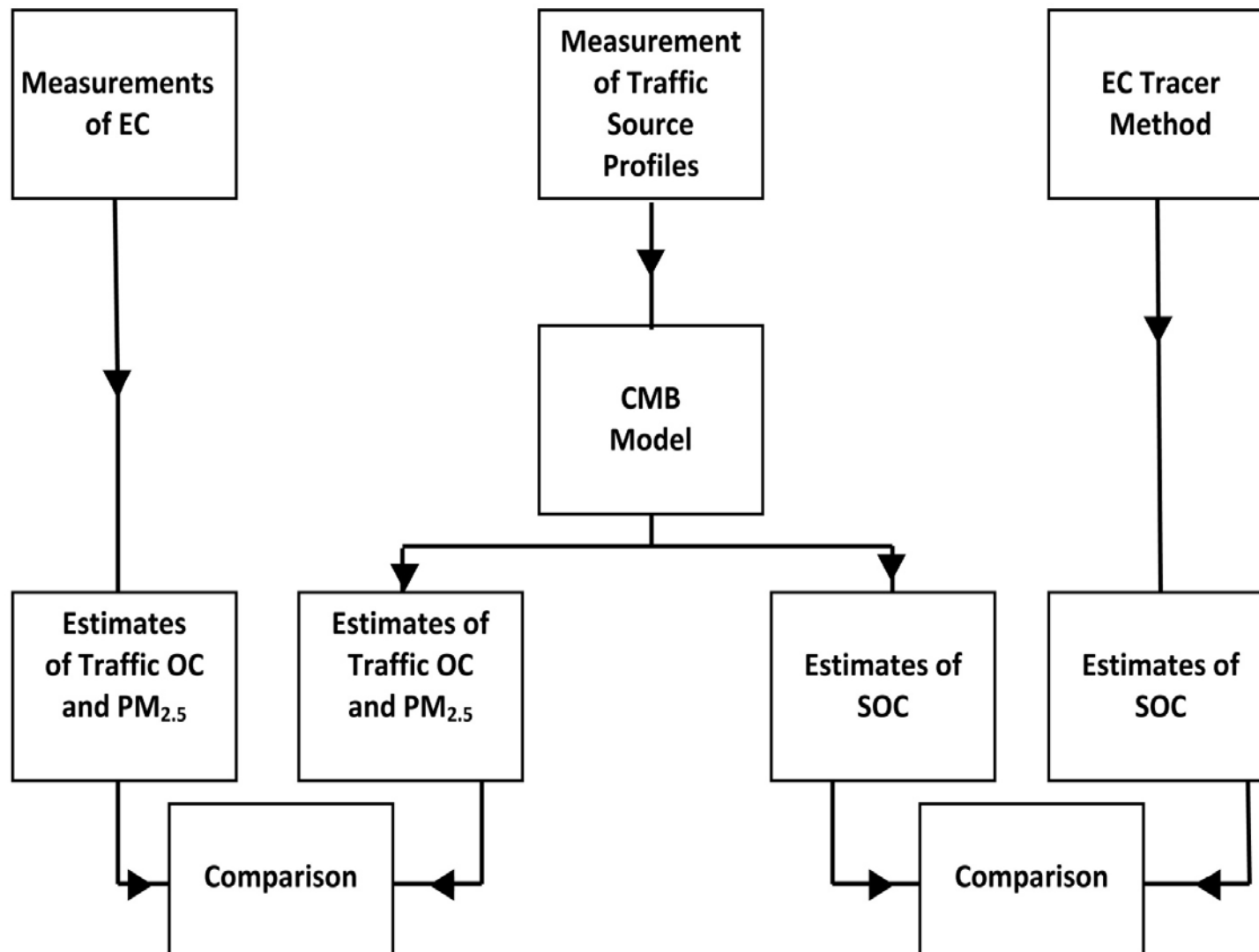


Figure 1: Assessment of model performance using different metrics

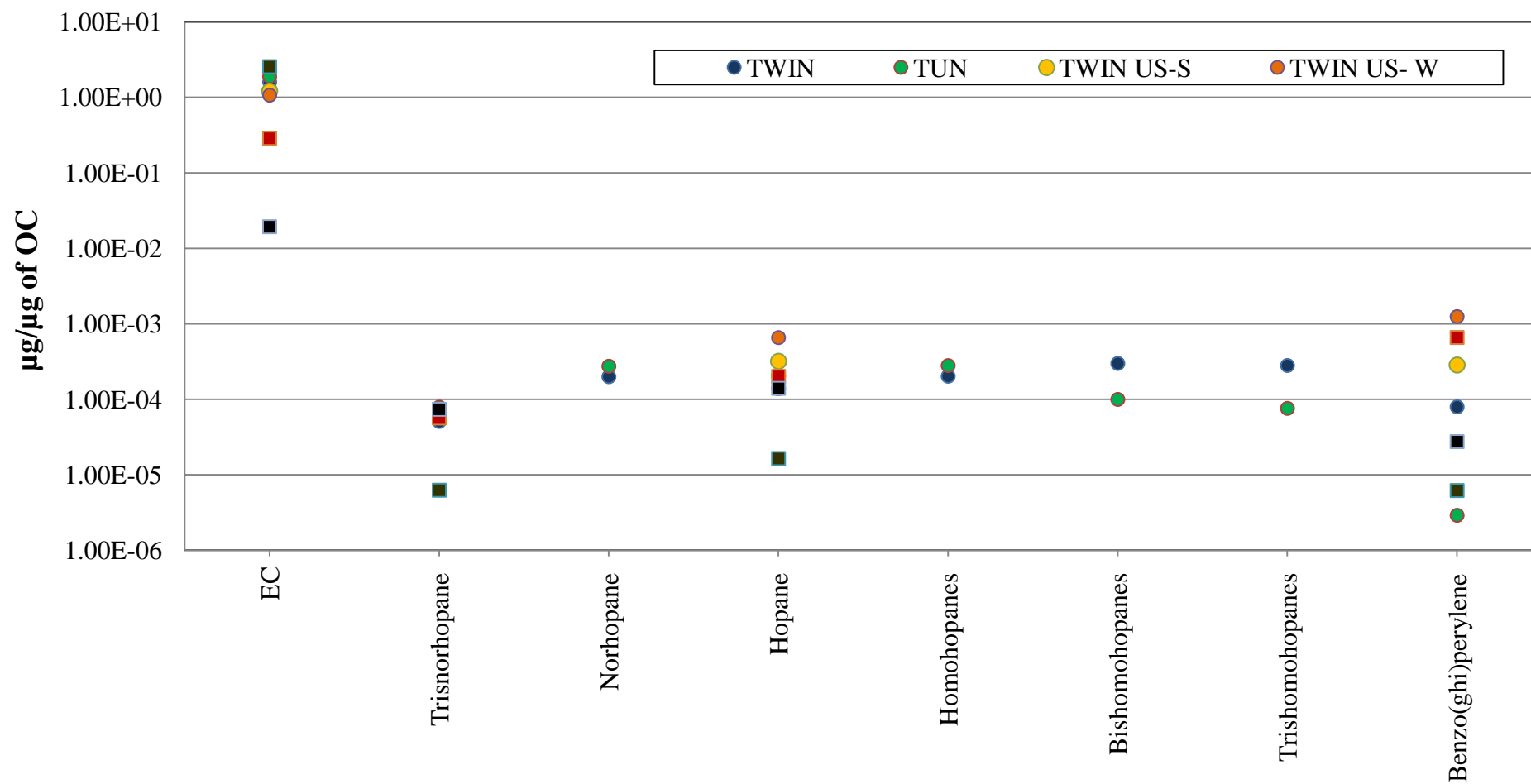
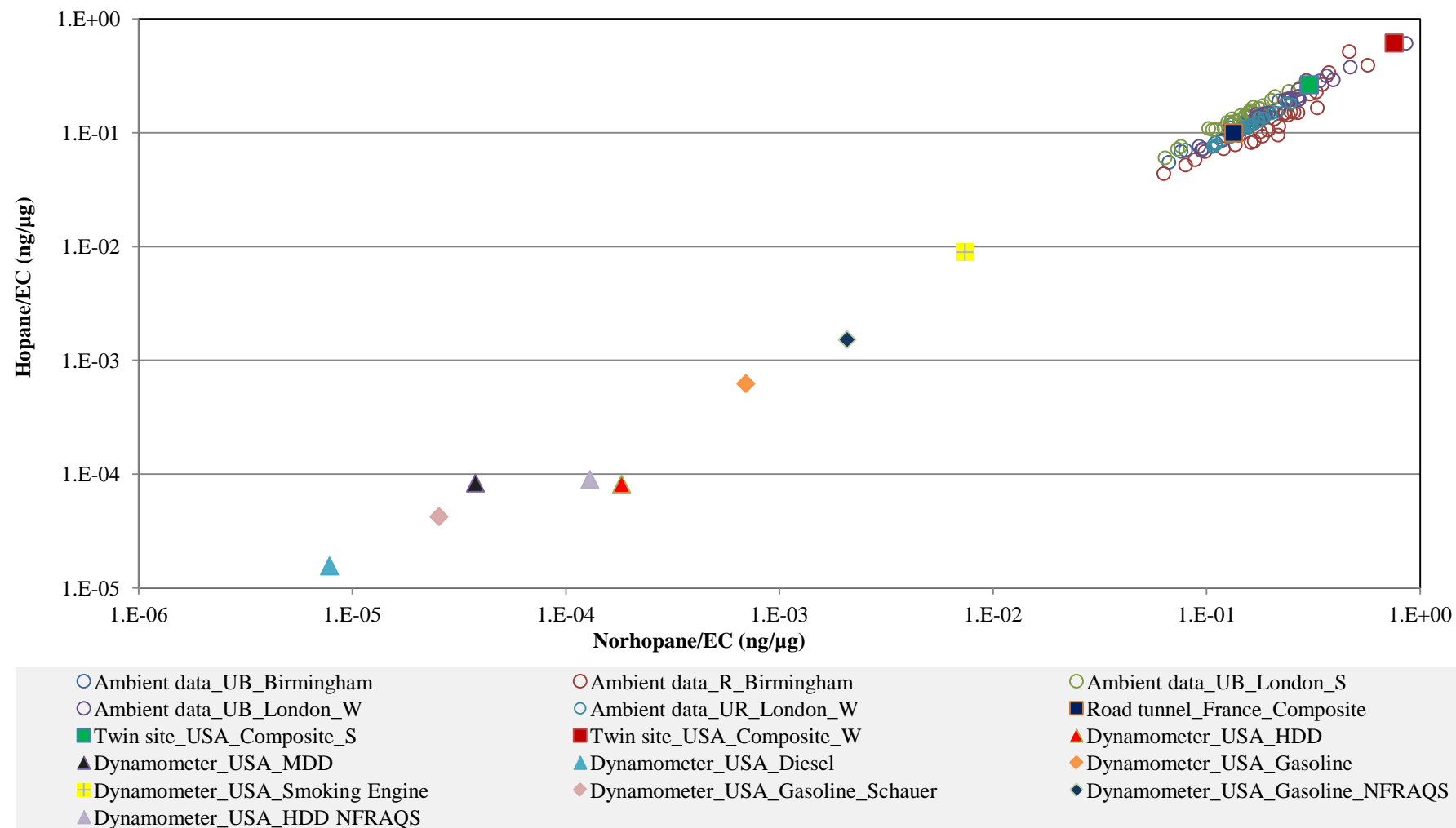
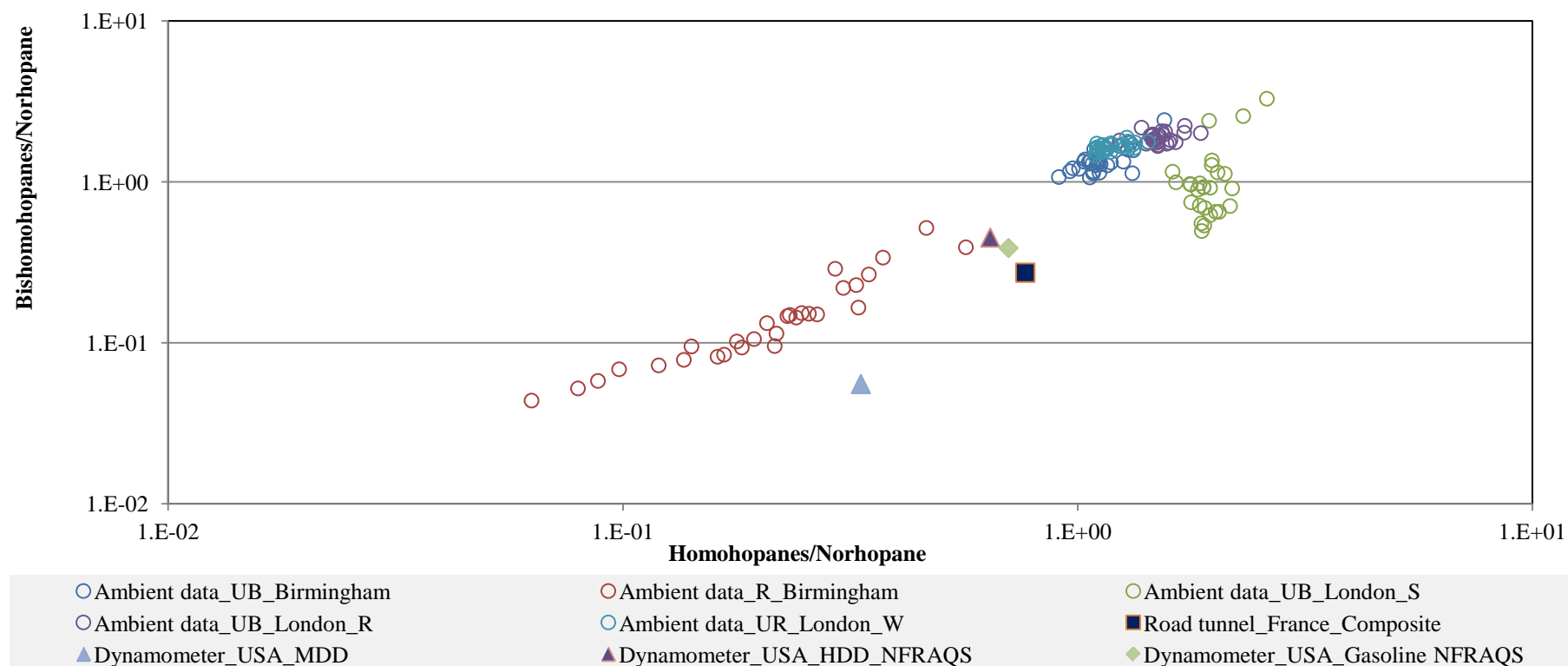


Figure 2: Comparison of London profile with other traffic and dynamometer profiles (TWIN- Our profile; TUN- El Haddad et al. (2009); TWIN US- S & W- Yan et al., 2009; DYN-D, G & S- Lough et al., 2007)

(a) Hopane-EC ratio-ratio plot



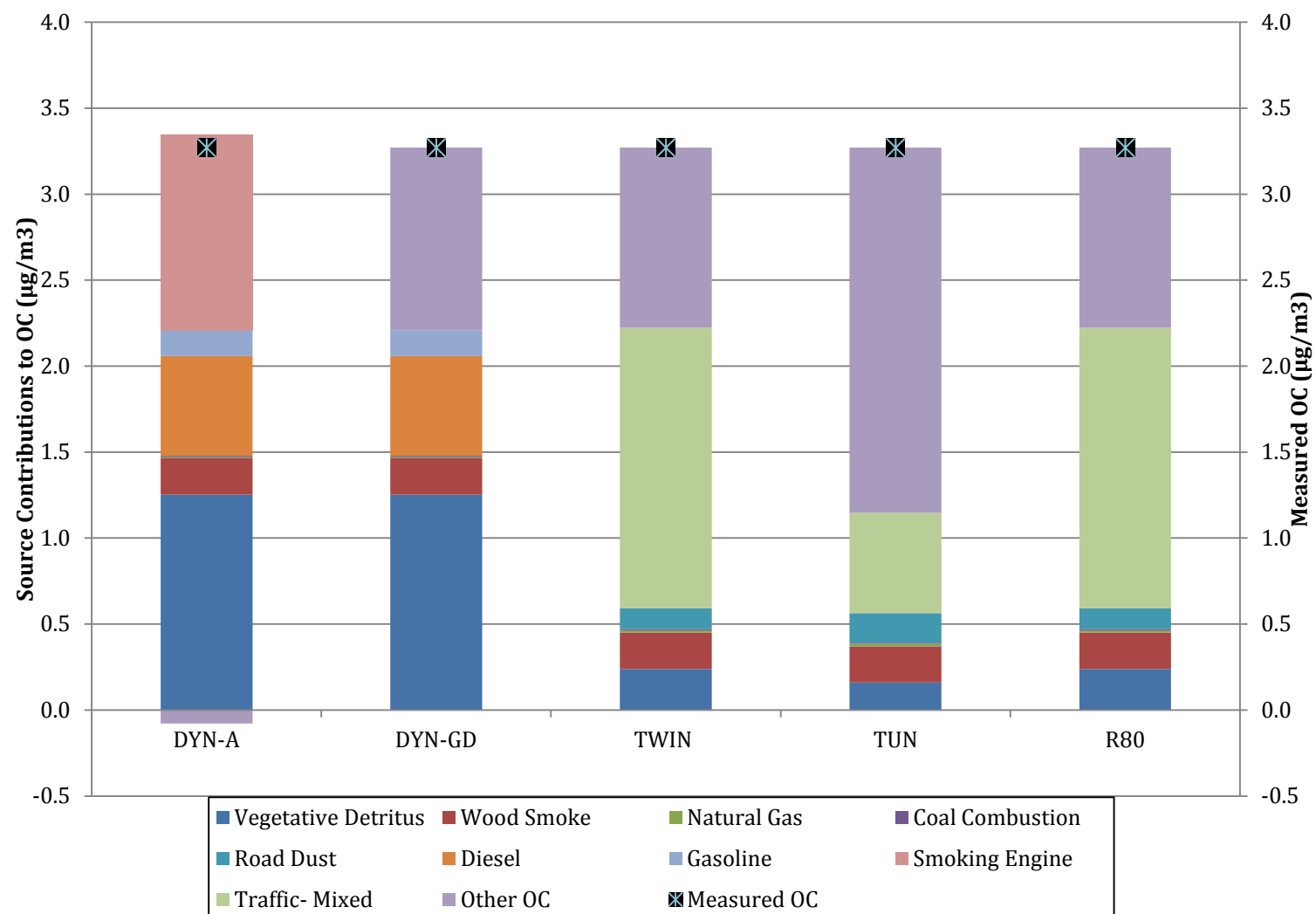
(b) Hopane- hopane ratio-ratio plot



o ambient data from current study; □ other ambient profiles; ◇ gasoline profile from dynamometer; Δ diesel profile from dynamometer; + smoking engine profile from dynamometer

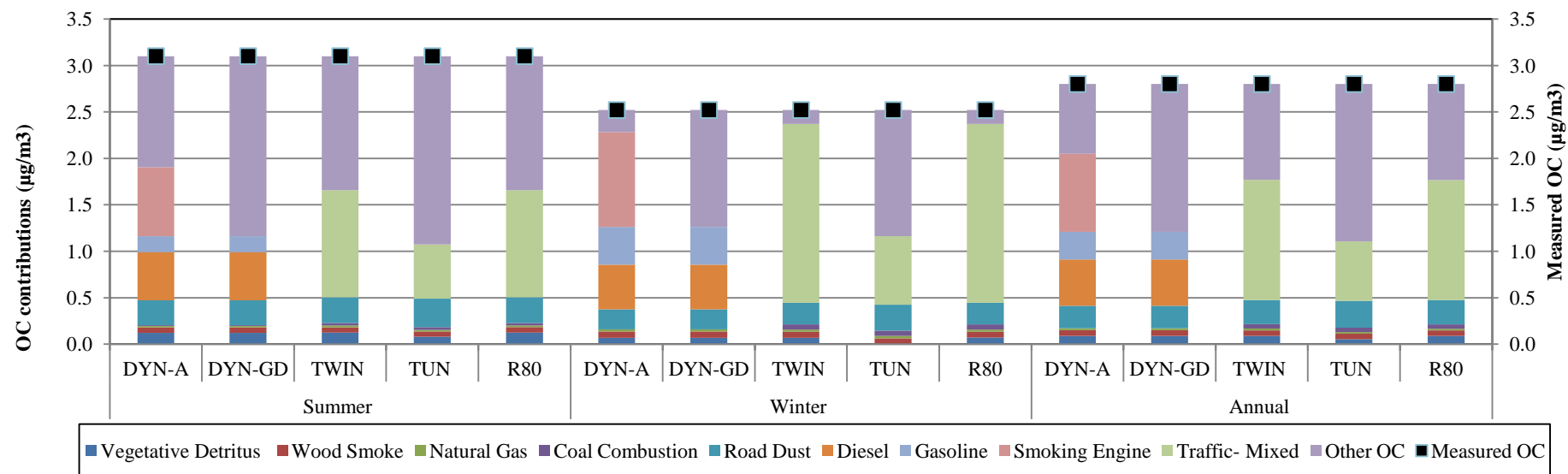
Figure 3: Comparison of source profiles derived from ambient air measurements and dynamometer studies using ratio-ratio plots

(a) London



(b) Birmingham

1. Urban background



2. Rural

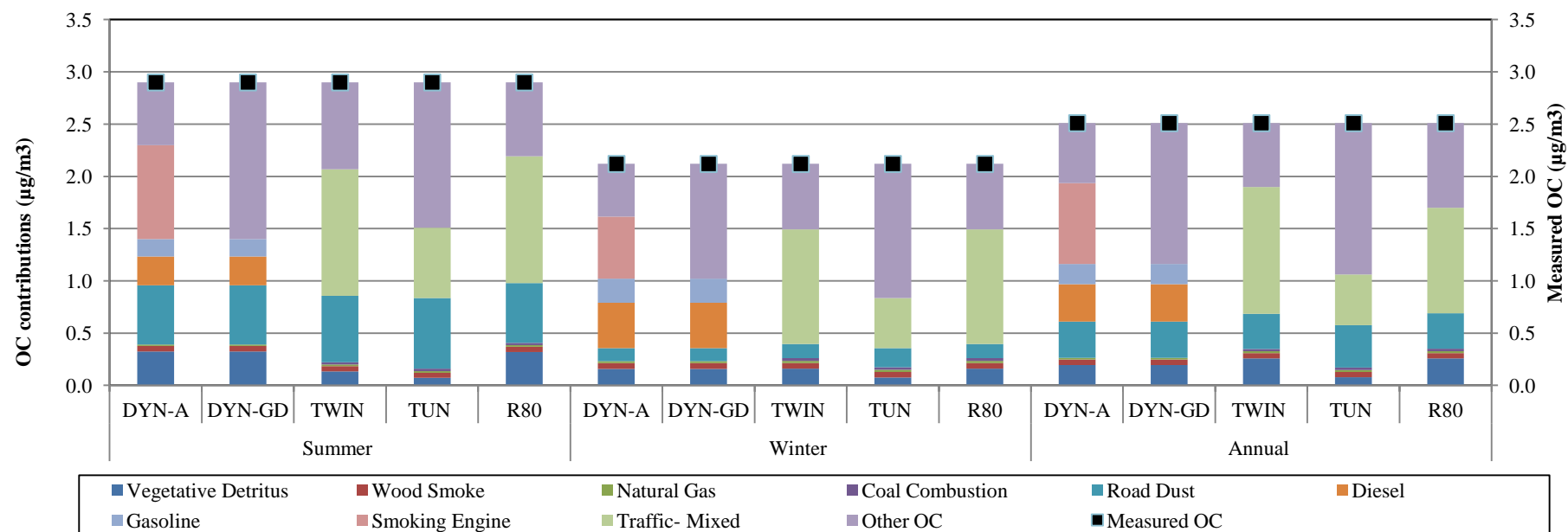
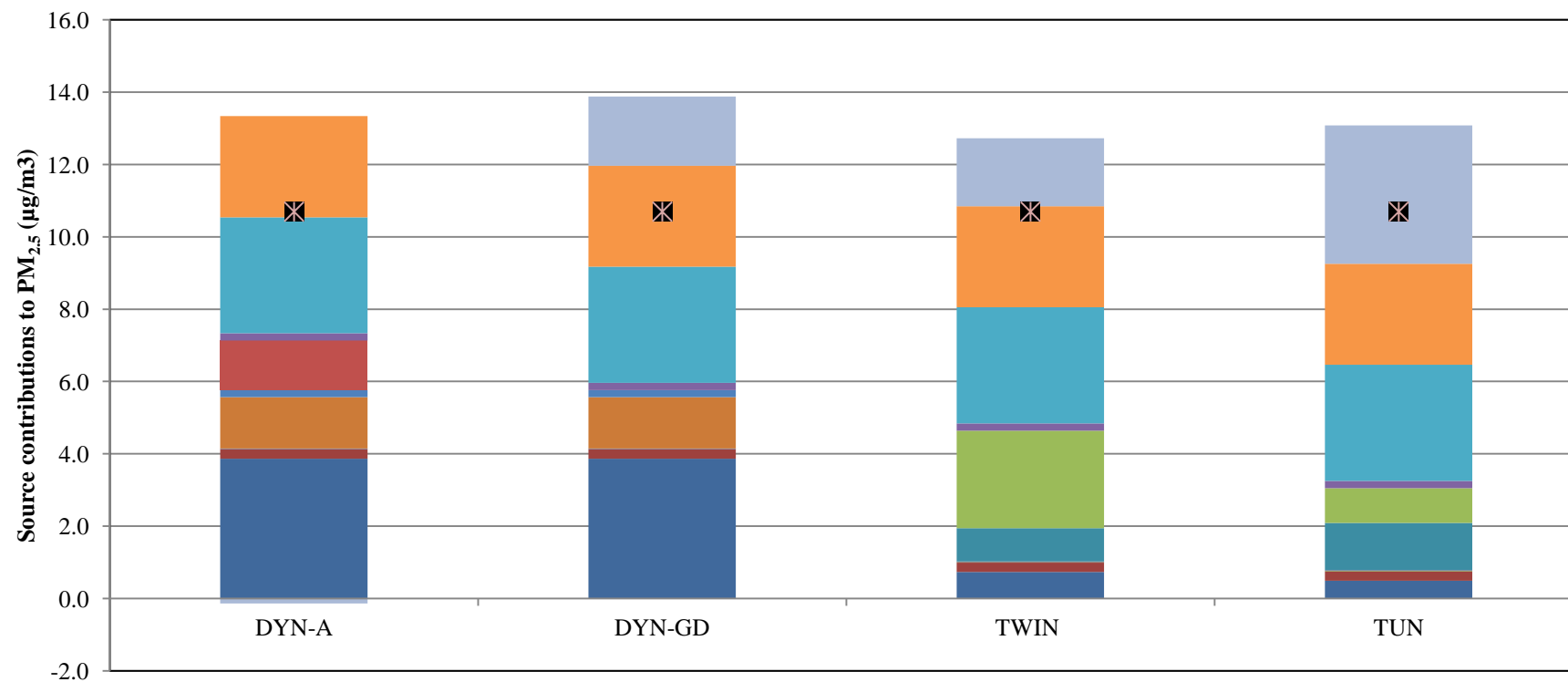


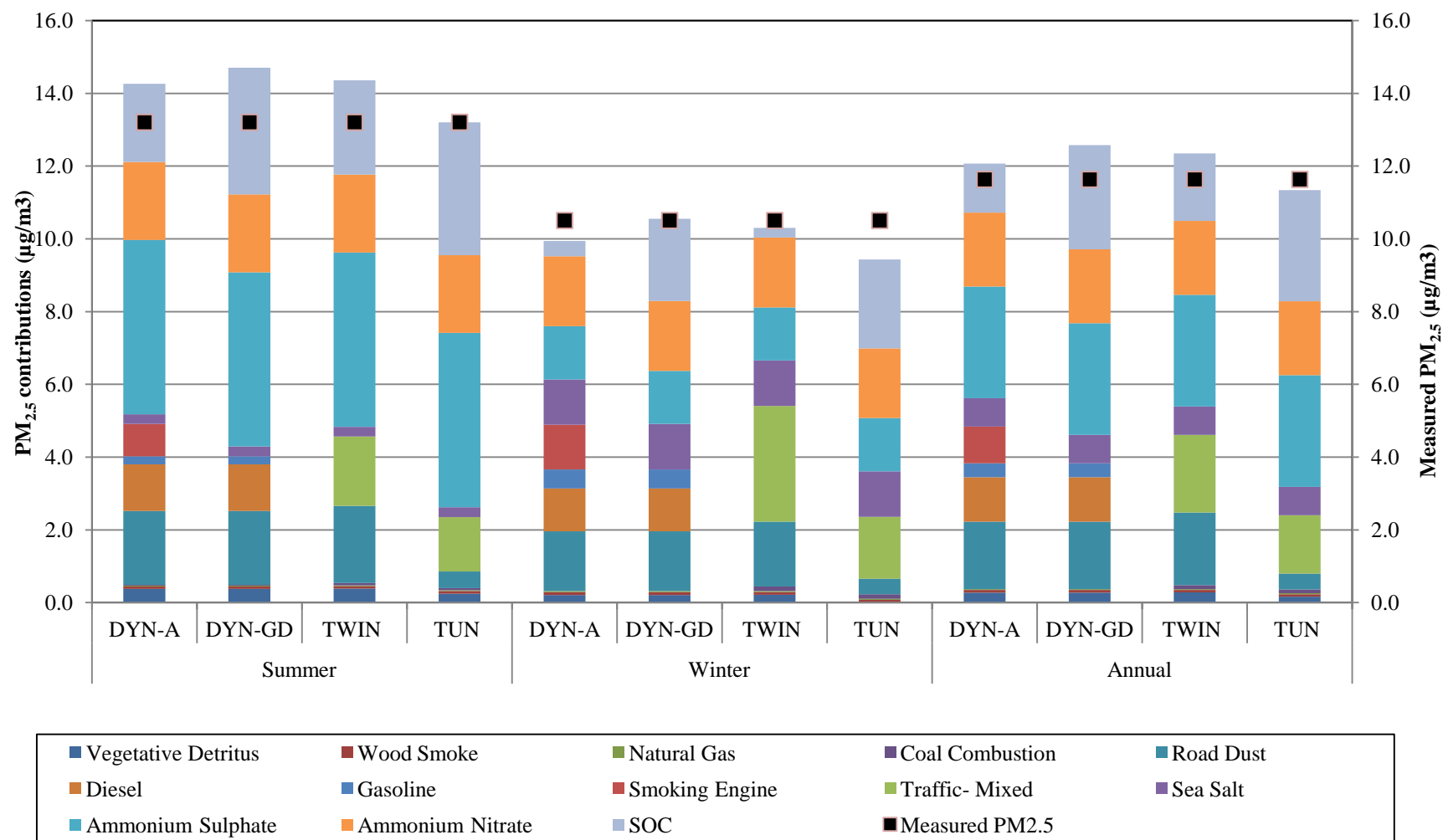
Figure 4: Source contribution estimates for organic carbon at different sites

(a) London



(b) Birmingham

1. Urban background



2. Rural

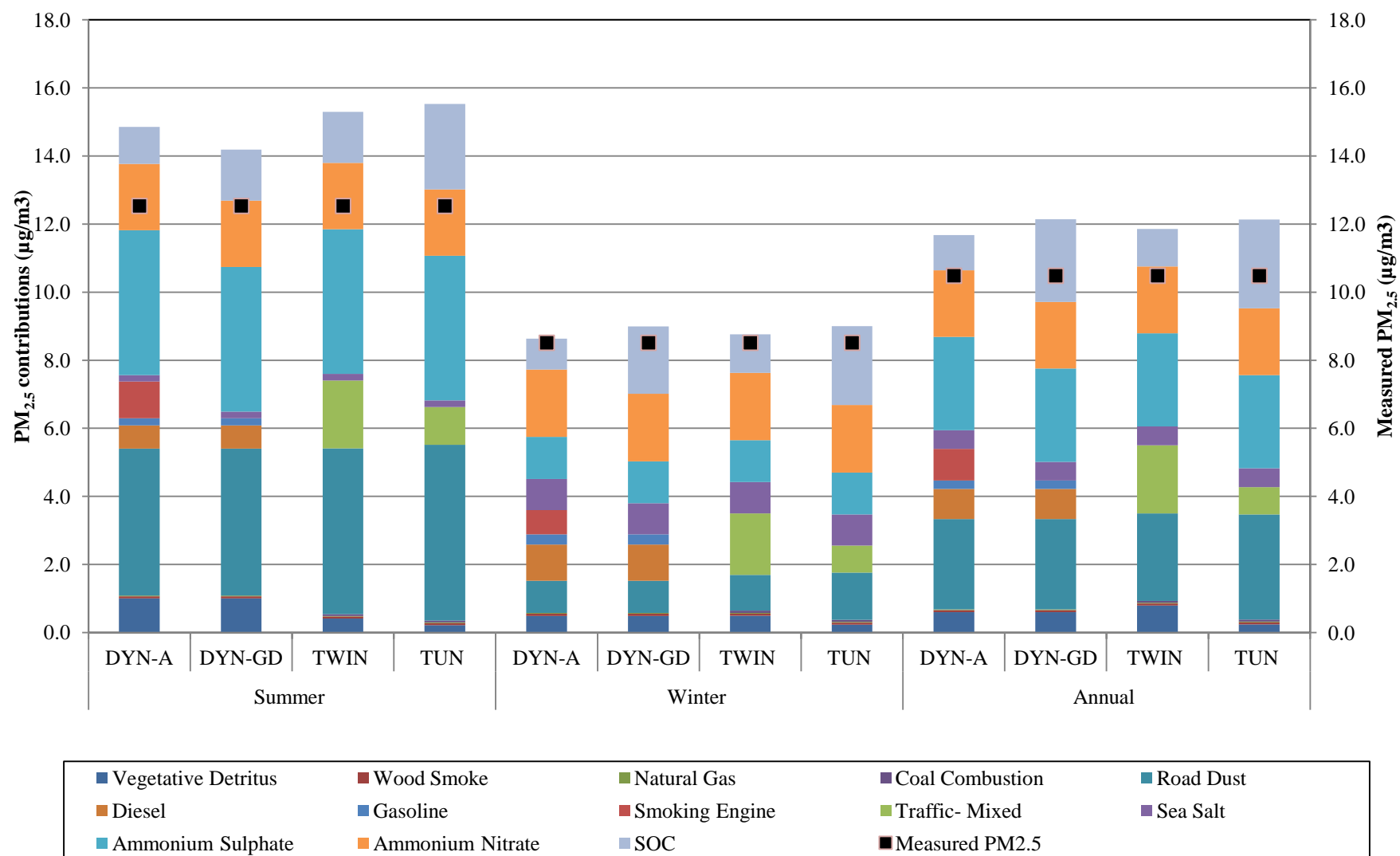


Figure 5: Source attribution of PM_{2.5} mass based on CMB results